Sonderdruck aus der Zeitschrift:

Berichte der Bunsen-Gesellschaft für physikalische Chemie (früher Zeitschrift für Elektrochemie)

Photoredox Reactions of the Binuclear Complex Ions $[(NC)_5Co(III)NCM(II)(CN)_5]^{6-}$ (M = Fe and Ru)

Arnd Vogler and Horst Kunkely

Fachbereich Chemie, Universität Regensburg, 84 Regensburg, Germany

Absorptionsspektren, sichtbar und ultraviolett / Komplexverbindungen / Photochemie

The electronic spectra of the complex ions $[(NC)_5Co(III)NCM(II)(CN)_5]^{6-}$ (M = Fe and Ru) exhibit absorption bands which are assigned to [Co(III) to M(II)] intervalence charge transfer (IT) transitions. There is strong evidence that upon irradiation of these bands the aqueous complexes underwent a redox reaction under formation of $Co(II)(CN)_5^{3-}$ and $M(III)(CN)_6^{3-}$. In the absence of oxygen these intermediates regenerated the starting complexes in a thermal redox reaction. This reaction was used to prepare the binuclear complexes. It is suggested that the photochemical redox reaction as well as its thermal reversal are closely related processes. This relationship is discussed on the basis of a theoretical model. The complex $Co(CN)_5^{3-}$ which is assumed to be formed as one of the primary products of the photolysis can be intercepted with oxygen. The analysis of the reaction products indicated that the reaction with oxygen produced $[(NC)_5CoO_2Co(CN)_5]^{6-}$ which underwent further reactions.

Die Elektronenspektren der Komplexionen $[(NC)_5Co(III)NCM(II)(CN)_5]^{6-}$ (M = Fe and Ru) besitzen Absorptionsbanden, die intervalence charge transfer (IT)-Übergängen vom Co(III) zum Fe(II) bzw. Ru(II) zugeordnet werden. Die Versuchsergebnisse stimmen mit der Annahme überein, daß die im Wasser gelösten Komplexe beim Bestrahlen dieser IT-Banden einer Redoxreaktion unter Bildung von $Co(II)(CN)_5^{3-}$ und $M(III)(CN)_6^{3-}$ unterlagen. Diese Zwischenprodukte bildeten in einer thermischen Redoxreaktion die Ausgangskomplexe zurück. Diese Reaktion diente auch zur Darstellung der zweikernigen Komplexe. Es wird angenommen, daß die photochemische Redoxreaktion und die thermische Rückreaktion verwandte Prozesse sind. Dieser Zusammenhang wird anhand eines theoretischen Modells diskutiert. Der Komplex $Co(CN)_5^{3-}$, der als eines der beiden primären Produkte der Photolyse gebildet wurde, kann mit Sauerstoff abgefangen werden. Aus der Analyse der Reaktionsprodukte kann man schließen, daß dabei zunächst der Komplex $[(NC)_5CoO_2Co(CN)_5]^{6-}$ gebildet wurde, der weiteren Reaktionen unterlag.

Introduction

It has been shown only recently that aqueous $[(NH_3)_5Co(III) \cdot NCRu(II)(CN)_5]^-$ underwent a photochemical redox decomposition under formation of Co^{2+} and $Ru(CN)_6^{3-}$ [1]. This reaction has been assumed to be induced by a direct optical electron transfer from Ru(II) to Co(III). Such an electronic transition has been termed intervalence charge transfer (IT) [2, 3]. The first aim of the present study was to show that this new type of photochemical redox reaction is not restricted to the example mentioned above. Second, the assumption that thermal and photochemical redox reactions between transition metal complexes are closely related processes [1] requires more experimental support. The complex ions $[(NC)_5Co(III)NCM(II)(CN)_5]^{6-}$ (M = Fe and Ru) were chosen for several reasons*). The binuclear complex $[(NC)_5Co(III)NCFe(II)(CN)_5]^{6-}$ is well known [5] and the preparation of the corresponding ruthenium compound was not anticipated to be difficult.

In these binuclear complexes the interaction of the reducing metal centers Fe(II) and Ru(II) with the oxidizing center Co(III) may lead to an M(II) to Co(III) IT transition at relatively low energies. The occurance of an IT transition which involves a complete exchange of an electron requires that both metal centers interact only weakly and exist in rather well defined oxidation states [3, 6]. Transitions between delocalized states which are formed by extensive mixing of electronic states of both metals are not IT transitions in a strict sense and difficult to assess experimentally. There are two simple criteria which may be used to establish the existence of trapped valencies. First, in addition to IT bands the electronic spectra should consist of the superimposed spectra of both mononuclear components which constitute the binuclear complex. Second, the energy of the vibration of certain ligands should not be changed upon incorporation of the mononuclear into a binuclear complex. In octahedral complexes the cyanide ligands are well suited to verify this requirement since the frequency of their stretching vibrations is a sensitive function of the oxidation state of the metal [7]. In analogy to the complexes $[(NH_3)_5Ru(II)pyrazineRu(III)(NH_3)_5]^{5+}$ [8], $[(NC)_5Fe(II)CNFe(III)(CN)_5]^{6-}$ [9], and $[(NH_3)_5Co(III) \cdot NCRu(II)(CN)_5]^-$ [1] also the ions $[(NC)_5Co(III)NCM(II) \cdot (CN)_5]^{6-}$ (M = Fe and Ru) are expected to contain weakly interacting metals.

The photochemistry of the aqueous mononuclear components which constitute these binuclear complexes has been investigated in several studies. At longer wavelengths the electronic spectra of $[Co(CN)_5X]^{3-}$ with X = CN, Cl, Br, J, NCS, SCN, N_3 exhibit less intense LF bands [10, 11]. Upon irradiation of the LF bands most of these complexes have been observed to undergo a substitution of X^- [10, 12, 13]. At shorter wavelengths the spectra show X^- to Co(III) CT absorptions [11]. It has been shown that upon CT excitation $[Co(CN)_5N_3]^{3-}$ underwent a redox reaction under formation of $Co(CN)_5^{3-}$ and an azide radical in the primary step [14]. The spectrum of $Fe(CN)_5^{4-}$ exhibits a LF band at 322 nm [15]. Upon irradiation of this absorption an aquation took place under formation of $[Fe(CN)_5H_2O]^{3-}$ [16]. The intense absorption at shorter wavelengths has been assigned to a [Fe(II) to CN^-]CT band of $Fe(CN)_6^{4-}$ [15]. In aqueous solution solvated electrons were produced upon irradiation of this CT band [17]. The corresponding observation has been made upon CT excitation of $Ru(CN)_6^{4-}$ [17].

If the interaction of both metals of $[(NC)_5Co(III)NCM(II) \cdot (CN)_5]^{6-}$ (M = Fe and Ru) leads to an IT transition the corresponding absorption band must occur at longer wavelengths than the CT bands of the mononuclear components to establish unambigously that the occurance of a photoredox reaction is indeed associated with an IT transition. For this reason the present investigation was restricted to the wavelength region above 300 nm where CT absorptions of the mononuclear components do not occur.

Experimental Section

Materials

$Ba_3[(NC)_5Co(III)NCFe(II)(CN)_5] \cdot 16H_2O$ [5] and $K_4Ru(CN)_6$ [18] were prepared according to the literature.

$K_6[(NC)_5Co(III)NCRu(II)(CN)_5] \cdot 8H_2O$. A solution of $K_3Ru(CN)_6$ was prepared by the oxidation of $Ru(CN)_6^{4-}$ with PbO_2. Diluted sulfuric acid was slowly added to a suspension of PbO_2 in an aqueous solution of $K_4Ru(CN)_6$. At the end of the reaction the addition of the acid has to be stopped because $Ru(CN)_5^{3-}$ decomposes quickly in acidic solution. Upon filtration an orange solution containing $Ru(CN)_6^{3-}$ was obtained. This solution was saturated with nitrogen and added to a solution of $K_3Co(CN)_5$ [5]. After 10 minutes ethanol was added. A precipitation took place. The precipitate which was sometimes obtained as an oil, was collected by filtration and recrystallized several times. Finally, an almost colorless solid was obtained. Anal. Calcd. for $K_6[(NC)_5Co(III) \cdot NCRu(II)(CN)_5] \cdot 8H_2O$; C, 16.01; N, 18,68; H, 1.94. Found: C, 16.17; N, 18.66; H, 1.83.

Photolysis Procedure

The light sources used were a 100 W Osram high-pressure mercury lamp and a Spectra Physics 165 argon laser. The following Schott interference filters of the type PIL were used for the irradiation at selected wavelengths: 313, 333, 366, and 436 nm. The filter combination Schott GG 400 and Balzers K1 transmitted light of the wavelength 405 nm. The filter Schott UG1 transmitted light between 320 and 380 nm. The laser emitted light of the wavelength 458 nm.

*) The photochemistry of $[(NC)_5CoNCFe(CN)_5]^{6-}$ has been recently investigated by Itoh [4]. His results and conclusions are discussed later in the present publication.

The photolyses were carried out at room temperature in a 10-cm cylindrical spectrophotometer cell, using concentrations of complex such as to have essentially complete light absorption. An aliquot of the solution to be analyzed was kept in the dark, at the same temperature, so that any thermal reaction could be noted and allowed for. However, correction for the thermal reaction was negligible. The total amount of photolysis was limited to less than 10% to avoid secondary photochemical reactions. Absorbed light intensities were determined by Ferrioxalate actinometry [19].

The solutions to be photolyzed were saturated either with nitrogen or with oxygen. The solvents were prepared by refluxing water in a stream of nitrogen or oxygen. The preparation and photolysis of the solutions saturated with nitrogen were carried out under exclusion of air. During the photolysis a stream of oxygen passed the solutions which were saturated with oxygen.

Measurements

Infrared spectra were measured with a Perkin Elmer 325 IR spectrophotometer. Samples were KBr pellets. Visible and ultraviolet spectra were measured in 1-cm cells with a Cary 14 recording spectrophotometer and a Zeiss PMQ II spectrophotometer for measurements at selected wavelengths.

Results

$[(NC)_5Co(III)NCFe(II)(CN)_5]^{6-}$. The electronic spectrum of $[(NC)_5Co(III)NCFe(II)(CN)_5]^{6-}$ (Fig. 1) exhibits two absorption maxima at 385 nm ($\varepsilon = 630$) and 326 nm ($\varepsilon = 820$) [5]. Upon irradiation of the first or the second band the aqueous binuclear complex underwent any photoreaction only after very long irradiation times if the solution was saturated with nitrogen. However, a very efficient photolysis took place if the solution was saturated with oxygen. Upon irradiation in alkaline solution (1 M KOH) the spectral changes which accompanied the photolysis (Fig. 2) clearly indicated the formation of $[(CN)_5CoO_2Co(CN)_5]^{5-}$ which exhibits a very intense absorption maximum at 310 nm ($\varepsilon = 24800$) [20]. This superoxo complex is assumed to be formed according to the following reaction scheme:

$$[(NC)_5Co(III)NCFe(II)(CN)_5]^{6-} \rightarrow [Co(II)(CN)_5]^{3-} + Fe(CN)_6^{3-} \quad (1)$$

(primary photochemical step)

$$2\,Co(CN)_5^{3-} + O_2 \rightarrow [(NC)_5Co(III)O_2Co(III)(CN)_5]^{6-} \quad (2)$$

$$[(NC)_5Co(III)O_2Co(III)(CN)_5]^{6-} + Fe(III)(CN)_6^{3-} \rightarrow [(NC)_5Co(III)O_2Co(III)(CN)_5]^{5-} + Fe(CN)_6^{4-} \quad (3)$$

$$2[(NC)_5Co(III)NCFe(II)(CN)_5]^{6-} + O_2 \rightarrow Fe(CN)_6^{3-} + Fe(CN)_6^{4-} + [(NC)_5Co(III)O_2Co(III)(CN)_5]^{5-} \quad (4)$$

(overall reaction)

The intermediates, which are presumably produced in the primary photochemical step (1), are expected to regenerate the starting complex [5]. However, if oxygen is present, $Co(CN)_5^{3-}$ may be intercepted under formation of the peroxo complex (2) [5, 20]. Reaction (3) is well known to proceed in alkaline solution [5]. The absorption of the superoxo complex is so intense that any other reaction product can not be identified in the spectrum of the photolyzed solution.

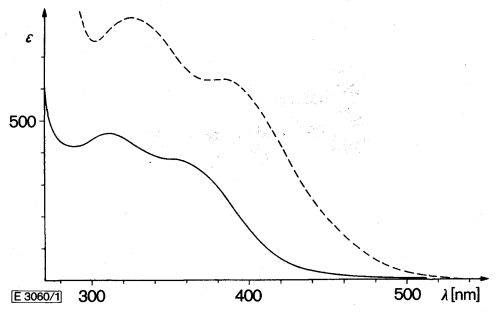

Fig. 1
Electronic spectra of aqueous $[(NC)_5Co(III)NCM(II)(CN)_5]^{6-}$ (M = Ru: ———; M = Fe: - - - - - -)

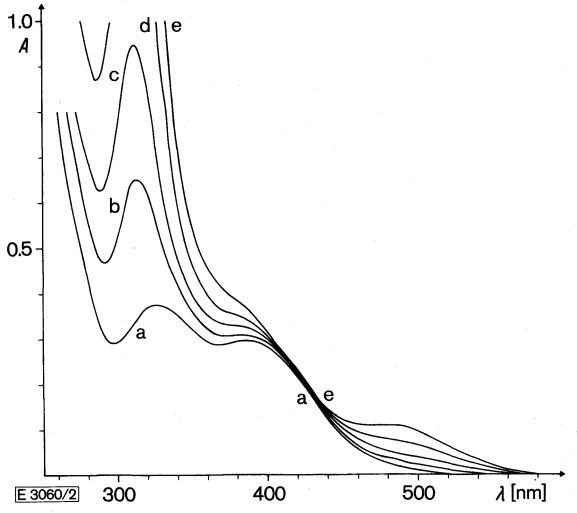

Fig. 2
Spectral changes during the photolysis of $4.75 \cdot 10^{-4}$ M $[(NC)_5Co(III)NCFe(II)(CN)_5]^{6-}$ in 1 M KOH saturated with oxygen, 366 nm irradiating wavelength. a: 0 min; b: 1 min; c: 2 min; d: 5 min; e: 10 min irradiation time

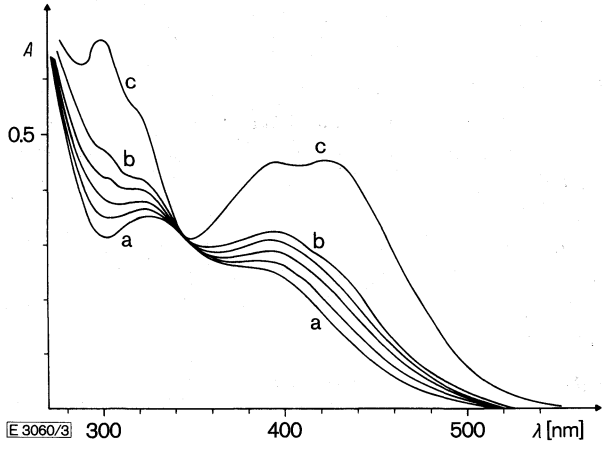

Fig. 3
Spectral changes during the photolysis of $4.15 \cdot 10^{-4}$ M $[(NC)_5Co(III)NCFe(II)(CN)_5]^{6-}$ in 10^{-4} M HCl saturated with oxygen, 366 nm irradiating wavelength, 20 sec irradiation periods, a: 0 sec; b: 80 sec irradiation time
c: $[(NC)_5Co(III)NCFe(III)(CN)_5]^{5-}$ obtained upon oxidation of $[(NC)_5Co(III)NCFe(II)(CN)_5]^{6-}$ (curve a) by H_2O_2

In a slightly acidic solution (10^{-4} M HCl) saturated with oxygen the photolysis of $[(NC)_5Co(III)NCFe(II)(CN)_5]^{6-}$ led to other reaction products. The spectral changes (Fig. 3) which were observed upon irradiation of the first or second absorption band indicated the formation of $Fe(CN)_6^{3-}$. Only at the beginning the reaction followed a zeroth order kinetics if light absorption by the starting complex was complete. Very soon the spectrum was obscured by the products of a secondary photolysis which was probably due to the known photoreactions of the strongly absorbing complex $Fe(CN)_6^{3-}$ [13, 16]. We assume that the primary photochemical step (1) and the subsequent formation of the peroxo complex (2) occured also in slightly acidic medium. The reaction should then proceed according to the following scheme:

$$[(NC)_5Co(III)O_2Co(III)(CN)_5]^{6-} + 2H^+ + 2H_2O \rightarrow 2[Co(III)(CN)_5H_2O]^{2-} + H_2O_2 \quad (5)$$

$$2[(NC)_5Co(III)NCFe(II)(CN)_5]^{6-} + 2H^+ + H_2O_2 \rightarrow 2H_2O + 2[(NC)_5Co(III)NCFe(III)(CN)_5]^{5-} \quad (6)$$

$$2[(NC)_5Co(III)NCFe(II)(CN)_5]^{6-} + 2H^+ + \tfrac{1}{2}O_2 \rightarrow Co(CN)_5H_2O^{2-} + Fe(CN)_6^{3-} + [(NC)_5Co(III)NCFe(III)(CN)_5]^{5-} \quad (7)$$

(overall reaction)

The reactions (5) [5, 20, 21] and (6) [5] are well known to take place in acidic solution. It follows that not only $Fe(CN)_6^{3-}$ but also $[(NC)_5Co(III)NCFe(III)(CN)_5]^{5-}$ should be detected in the spectrum of the photolyzed solution, whereas the identification of $Co(CN)_5H_2O^{2-}$ is difficult due to the low intensity of its absorption bands [5, 10, 13]. However, since the primary photolysis could not be driven very far the spectral changes are too small for an unambigous discrimination between $Fe(CN)_6^{3-}$ and $[(NC)_5Co(III)NCFe(III)(CN)_5]^{5-}$. Actually, the spectra of $[(NC)_5Co(III)NCFe(III)(CN)_5]^{5-}$ (Fig. 3) and of a mixture of $Co(CN)_5H_2O^{2-}$ and $Fe(CN)_6^{3-}$ are quite similar since also the spectrum of the oxidized binuclear complex [5] is dominated by the intense absorptions of $Fe(CN)_6^{3-}$ [15]. The band maxima of $Fe(CN)_6^{3-}$ (420 nm, $\varepsilon = 1050$; 301 nm, $\varepsilon = 1600$) and of $[(NC)_5Co(III)NCFe(III)\cdot(CN)_5]^{5-}$ (422 nm, $\varepsilon = 1080$; 300 nm, $\varepsilon = 1700$) appear almost at the same wavelengths and have nearly the same intensities. This observation was used for the determination of the quantum yield of the sum of $Fe(CN)_6^{3-}$ and $[(NC)_5Co(III)NCFe(III)(CN)_5]^{5-}$ at different irradiating wavelengths:

irradiating wavelength	333 nm	366 nm	405 nm	436 nm	458 nm
quantum yield	0.8	1.1	1.6	1.2	0.5

$[(NC)_5Co(III)NCRu(II)(CN)_5]^{6-}$. The electronic spectrum of $[(NC)_5Co(III)NCRu(II)(CN)_5]^{6-}$ (Fig. 1) exhibits two absorption maxima at 350 nm ($\varepsilon = 380$) and 312 nm ($\varepsilon = 460$). Upon irradiation of the first or the second band aqueous $[(NC)_5Co(III)NCRu(II)CN_5]^{6-}$ underwent a photochemical reaction even if the solution was saturated with nitrogen. In slightly acidic medium (10^{-4} M HCl) the absorption of light into the band at longer wavelengths led to a spectral change (Fig. 4) which clearly indicated a photoaquation under formation of $Co(CN)_5H_2O^{2-}$ and $Ru(CN)_6^{4-}$. At the isosbestic point at 392 nm the starting complex and $Co(CN)_5H_2O^{2-}$ have the same extinction coefficient ($\varepsilon = 210$). $Ru(CN)_6^{4-}$ absorbs only below 300 nm [22, 23]. Since the absorption spectra of the starting complex and of $Co(CN)_5H_2O^{2-}$ are known [5, 10, 13] the change of the extinction above 300 nm was used to determine the concentration of $Co(CN)_5H_2O^{2-}$. The quantum yield of this aquation was $\phi = 0.26$ at 405 nm irradiating wavelength.

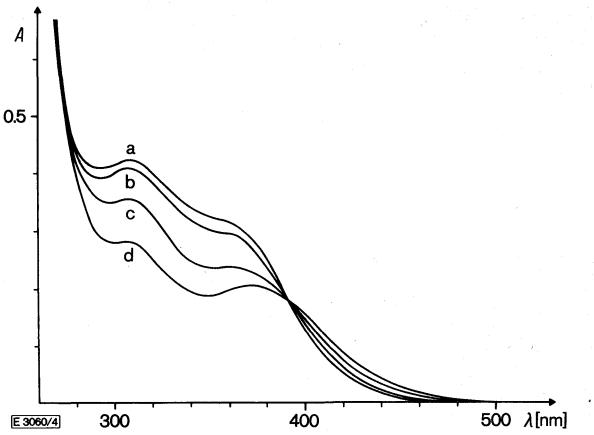

Fig. 4
Spectral changes during the photolysis of $8.5 \cdot 10^{-4}$ M $[(NC)_5Co(III)NCRu(II)(CN)_5]^{6-}$ in 10^{-4} M HCl saturated with nitrogen, 405 nm irradiating wavelength, a: 0 min; b: 15 min; c: 60 min; d: 120 min irradiation time

If the photolysis was carried out in the presence of oxygen the spectral changes were similar to those which occured in a solution saturated with nitrogen. But a clear isosbestic point did not appear. This observation could be due to the interference of the products of a photoredox reaction which might take place with low efficiency in addition to the photoaquation. Such a photoredox reaction should proceed in analogy to the corresponding iron complex. This assumption is supported by the observation that in alkaline solution (1 M KOH) the photolysis of $[(NC)_5Co(III)NCRu(II)(CN)_5]^{6-}$ led to the formation of the superoxo complex $[(NC)_5CoO_2Co(CN)_5]^{5-}$ which can be identified even at very low concentrations due to its extremly intense absorption at 310 nm. The increase of the extinction at this wavelength was used to determine the concentration of the superoxo complex formed upon irradiation. The interference by other reaction products was neglected since they have much smaller extinction coefficients. In an alkaline solution (1 M KOH) saturated with oxygen $[(NC)_5CoO_2Co(CN)_5]^{5-}$ was formed with the quantum yield $\phi = 0.02$ at 405 nm irradiating wavelength. Under the same conditions upon irradiation of the band at shorter wavelengths the spectral changes (Fig. 5) indicated an efficient formation of the superoxo complex. At 313 nm irradiating wavelength the quantum yield was $\phi = 0.39$.

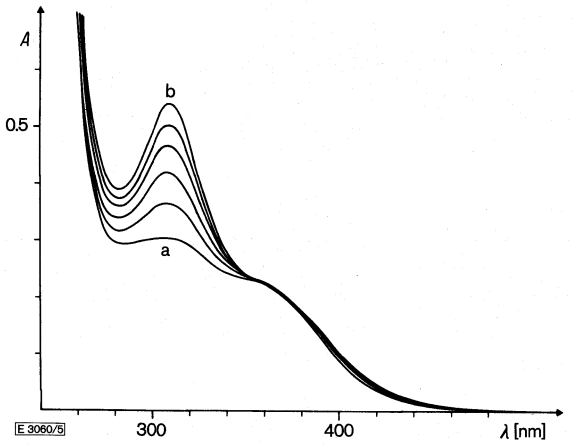

Fig. 5
Spectral changes during the photolysis of $6.2 \cdot 10^{-4}$ M $[(NC)_5Co(III)NCRu(II)(CN)_5]^{6-}$ in 1 M KOH saturated with oxygen, irradiating wavelength between 320 and 380 nm, 20 sec irradiation periods, a: 0 sec; b: 100 sec irradiation time

If this irradiation of the band at shorter wavelengths was carried out in slightly acidic solution (10^{-4} M HCl), the change of the spectrum followed a complicated pattern. This observation is probably due to the lability of $Ru(CN)_6^{3-}$ in acidic solution [22]. $Ru(CN)_6^{3-}$ should have been formed in analogy to the corresponding iron complex.

Discussion

$[(NC)_5Co(III)NCFe(II)(CN)_5]^{6-}$. The IR spectrum of $[(NC)_5Co(III)NCFe(II)(CN)_5]^{6-}$ exhibits three absorptions in the cyanide stretching region [7]. These bands have been assigned to the terminal cyanides coordinated to Co(III) ($2130\,cm^{-1}$) and Fe(II) ($2055\,cm^{-1}$), and to the bridging cyanide ($2090\,cm^{-1}$). The absorptions of these terminal cyanides appear at nearly the same wavenumbers as those of $Fe(CN)_6^{4-}$ ($2047\,cm^{-1}$) and Co(III) cyanide complexes ($2130\,cm^{-1}$). Since the energy of the cyanide stretching vibration is a sensitive function of the valency of the central metal it is concluded that both metals of $[(NC)_5Co(III) \cdot \cdot NCFe(II)(CN)_5]^{6-}$ exist in discrete oxidation states and interact only weakly.

The electronic spectrum of $[(NC)_5Co(III)NCFe(II)(CN)_5]^{6-}$ (Fig. 1) should then consist of the superimposed spectra of $Fe(CN)_6^{4-}$ and $Co(CN)_5NC^{3-}$ of IT bands would not occur. The long-wavelength absorption of $Fe(CN)_6^{4-}$ at 322 nm ($\varepsilon = 302$) has been assigned to the lowest spin-allowed LF transition [15]. $Co(CN)_5NC^{3-}$ is not a stable complex [24]. But it has been shown that the LF strength of a bridging cyanide coordinated via nitrogen compares well with that of ammonia [25–27]. $Co(CN)_5NH_3^{2-}$ exhibits its long-wavelength absorption at 346 nm ($\varepsilon = 230$) [28]. Hence the longest-wavelength band of the $Co(III)(CN)_5NC$-moiety should also appear as lowest-energy absorption in the spectrum of the binuclear complex. However, neither the wavelength (385 nm) nor the intensity ($\varepsilon = 630$) of the maximum of the long-wavelength band of $[(NC)_5Co(III)NCFe(II)(CN)_5]^{6-}$ can be explained by the assumption that the spectrum of the binuclear complex is composed of the spectra of both mononuclear components. We suggest, that the long-wavelength band of $[(NC)_5Co(III)NCFe(II)(CN)_5]^{6-}$ belongs to the lowest optical [Fe(II) to Co(III)] IT transition. This transition is assumed to be associated with the transfer of an electron from an t_{2g} state of Fe(II) to an e_g state of Co(III) (in O_h-symmetry). Since such a "te" type transition is forbidden the intensity of the corresponding absorption is rather low compared to other CT bands [29]. Our assignment is supported by the photochemical behavior of the complex.

In analogy to other Co(III) cyano complexes [10, 12, 13] aqueous $[(NC)_5Co(III)NCFe(II)(CN)_5]^{6-}$ should undergo a photoaquation under formation of $Co(CN)_5H_2O^{2-}$ and $Fe(CN)_6^{4-}$ upon irradiation of the long-wavelength band if this absorption would belong to the lowest LF transition of the binuclear complex. However, the results show that this reaction took place only with a very low efficiency if it occured at all. $[(NC)_5Co(III)NCFe(II)(CN)_5]^{6-}$ did apparently not undergo any efficient chemical change if oxygen was excluded. It is assumed that the irradiation led to a redox reaction under formation of $Co(II)(CN)_5^{3-}$ and $Fe(III)(CN)_6^{3-}$. But these intermediates should simply regenerate the starting complex in a well known thermal redox reaction [5]. This assumption is supported by the observation that $Co(II)(CN)_5^{3-}$ can be intercepted with oxygen. A reaction scheme is proposed which accounts for the photolysis products which are formed in the presence of oxygen. The secondary thermal reactions which follow the primary photochemical step are dependent on the acidity of the solution. Quantum yields were determined for the formation of $Fe(CN)_6^{3-}$ (and $[(NC)_5Co(III) \cdot \cdot NCFe(III)(CN)_5]^{5-}$) in acidic solution. According to the reaction scheme these measured quantum yields are not only dependent on the quantum yield of the primary photochemical step but include also the efficiency of the subsequent thermal reactions. The highest quantum yield was obtained upon irradiation of the long-wavelength band at its maximum. This observation is consistent with the assumption that this absorption is indeed an IT band.

In the absence of oxygen the intermediates which are formed in the primary photochemical reaction of $[(NC)_5Co(III) \cdot \cdot NCFe(II)(CN)_5]^{6-}$ simply regenerate the starting complex in a thermal redox reaction [5]:

$$[(NC)_5Co(III)NCFe(II)(CN)_5]^{6-} \underset{\text{thermal}}{\overset{h\nu}{\rightleftarrows}} Co(CN)_5^{3-} + Fe(CN)_6^{3-}$$

The photochemical redox reaction as well as its thermal reversal may be explained on a common basis by the theory advanced by N. S. Hush [3, 30]. A qualitative potential curve diagram (Fig. 6) shows the IT states and IT transitions which should be involved in these reactions. Curve A represents the electronic ground state of $[(NC)_5Co(III)NCFe(II)(CN)_5]^{6-}$ and curve B the ground state of $[(NC)_5Co(II)NCFe(III) \cdot \cdot (CN)_5]^{6-}$ with Co(II) in a low spin configuration as expected for a Co(II)-cyano complex [31]. The increase of the internuclear distance should reflect the strong Jahn-Teller distortion which is expected and has been observed to occur in low spin octahedral Co(II) complexes [32]. This influence could be so strong that $[(NC)_5Co(II)NCFe(III)(CN)_5]^{6-}$ may completely dissociate into $Fe(CN)_6^{3-}$ and $Co(CN)_5^{3-}$. The activation

energy of the thermal redox reaction (III in Fig. 6) which leads to the formation of $[(NC)_5Co(III)NCFe(II)(CN)_5]^{6-}$ is certainly very small [5]. But the activation energy which is required for the thermal reversal of this reaction (I in Fig. 6) is apparently rather high since $[(NC)_5Co(III)NCFe(II)(CN)_5]^{6-}$ is a thermally stable complex. However, this reaction can be achieved by the absorption of light which induces the optical IT transition (II in Fig. 6).

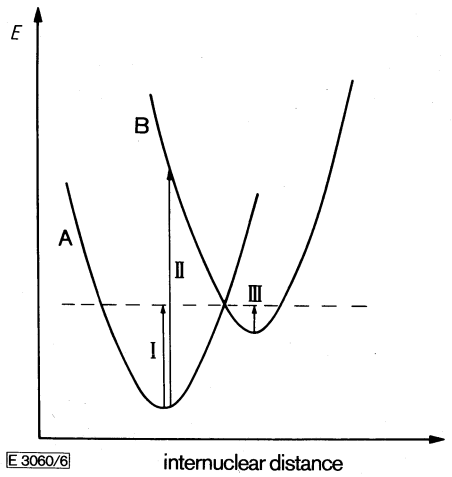

Fig. 6
Potential curve diagram of electronic IT states of $[(NC)_5Co(III)NCFe(II)(CN)_5]^{6-}$.
A $Co(III)t_{2g}^6$, $Fe(II)t_{2g}^6$; B $Co(II)t_{2g}^6e_g^1$, $Fe(III)t_{2g}^5$; I, III activation energies of the thermal redox reactions

$[(NC)_5Co(III)NCFe(II)(CN)_5]^{6-} \xrightarrow{h\nu_{II}} [(NC)_5Co(II)NCFe(III)(CN)_6]^{6-}$
II optical IT transition

Finally, some remarks have to be made to the results of Itoh who also investigated the photochemistry of $[(NC)_5Co(III)NCFe(II)(CN)_5]^{6-}$ but obtained different results [4]. He concluded that the primary photolysis led only to the formation of $[(NC)_4(H_2O)Fe(II)CNCo(III)(CN)_5]^{5-}$. He observed a change of the absorption spectrum upon irradiation of $[(NC)_5Co(III)NCFe(II)(CN)_5]^{6-}$ in a deaerated acidic solution. This spectral change is similar to that we found in the present study (Fig. 3). At 420 nm Itoh observed an increase of the optical density from about 0.6 to 0.9 after two hours of irradiation. Under comparable conditions he found only 10^{-5} Mol/l free cyanide released by the complex. A rough calculation shows then, that at 420 nm $[(NC)_4(H_2O)Fe(II)\cdot\cdot CNCo(III)(CN)_5]^{5-}$ should have an extinction coefficient of about $\varepsilon = 30000$ compared to $\varepsilon = 410$ for the starting complex. There is no obvious explanation for this difference. We assume that the spectral change observed by Itoh is due to the formation of $Fe(CN)_6^{3-}$ and $[(NC)_5Co(III)NCFe(III)\cdot\cdot(CN)_5]^{5-}$ caused by the presence of a small amount of oxygen which are difficult to remove. As soon as some $Fe(CN)_6^{3-}$ is formed it starts to absorb strongly due to its high extinction and undergoes a secondary photolysis under decomposition and release of cyanide [13]. Some of the other results of Itoh as for example the dependence of the photochemical reaction on the acidity of the solution can be also explained by our reaction scheme.

$[(NC)_5Co(III)NCRu(II)(CN)_5]^{6-}$. In the cyanide stretching region the IR spectrum of $[(NC)_5Co(III)NCRu(II)(CN)_5]^{6-}$ is very similar to that of the corresponding Fe(II) complex. The bridging cyanide absorbs at 2085 cm^{-1} and terminal cyanides at 2128 cm^{-1} and 2052 cm^{-1}. This latter absorption compares well with that of $Ru(CN)_6^{4-}$ at 2050 cm^{-1} [1]. It is again concluded that both metals interact only weakly.

The electronic spectrum of $[(NC)_5Co(III)NCRu(II)(CN)_5]^{6-}$ (Fig. 1) exhibits two absorption maxima at 350 nm ($\varepsilon = 380$) and 321 nm ($\varepsilon = 460$). Since $Ru(CN)_6^{4-}$ absorbs only below 300 nm [22, 23] all bands at longer wavelengths should belong to LF transitions of Co(III) and possibly to [Ru(II) to Co(III)] IT transitions. We assign the long-wavelength band to the lowest LF transition of the $Co(CN)_5NC$-moiety of the binuclear complex. The wavelength of the band maximum compares well with that of $Co(CN)_5NH_3^{2-}$ (346 nm) [28]. The extinction coefficient of the binuclear complex is higher than that of $Co(CN)_5NH_3^{2-}$ ($\varepsilon = 230$) at this wavelength. But this is certainly due to the overlap of two bands in the spectrum of the binuclear complex (Fig. 1). The short-wavelength band of $[(NC)_5Co(III)NCRu(II)(CN)_5]^{6-}$ at 312 nm is assigned to the lowest [Ru(II) to Co(III)] IT transition. This IT transition is expected and observed to occur at higher energies than that of the corresponding Fe(II) complex because $Ru(CN)_6^{4-}$ is much weaker reducing than $Fe(CN)_6^{4-}$ [22]. Our assignments of both absorption bands of $[(CN)_5Co(III)\cdot\cdot NCRu(II)(CN)_5]^{6-}$ are supported by the photochemical behaviour of this complex.

Upon irradiation of the IT band $[(NC)_5Co(III)NCRu(II)\cdot\cdot(CN)_5]^{6-}$, dissolved in an alkaline solution (1 M KOH) saturated with oxygen, underwent a redox reaction in analogy to the corresponding iron complex. At 313 nm irradiating wavelength $[(NC)_5CoO_2Co(CN)_5]^{5-}$ was formed with the quantum yield $\phi = 0.39$. Upon irradiation of the LF band at longer wavelengths the redox reaction was much less efficient. At 405 nm irradiating wavelength the superoxo complex was formed with the quantum yield $\phi = 0.02$. The main reaction was now a photoaquation under formation of $Co(CN)_5H_2O^{2-}$ and $Ru(CN)_6^{4-}$. At 405 nm irradiating wavelength the quantum yield of the formation of $Co(CN)_5H_2O^{2-}$ was 0.26.

The model which was used to describe the IT interaction in $[(NC)_5Co(III)NCFe(II)(CN)_5]^{6-}$ (Fig. 6) should also apply to the corresponding ruthenium complex. However, since $Ru(CN)_6^{4-}$ is less reducing than $Fe(CN)_6^{4-}$ [22] curve B (Fig. 6) will be shifted to higher energies if Fe(II) is replaced by Ru(II). It follows that also the optical IT transition (II in Fig. 6) requires more energy. The corresponding absorption band should then be shifted to shorter wavelengths compared to the iron complex. Such a shift was indeed observed.

Acknowledgment

Support for this research by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

References

[1] A. Vogler and H. Kunkely, Ber. Bunsenges. physik. Chem., in print.
[2] G. C. Allen and N. S. Hush, Progr. inorg. Chem. *8*, 357 (1967).

[3] N. S. Hush, Progr. inorg. Chem. *8*, 391 (1967).
[4] H. Itoh, Nippon Kagaku Kaishi 2349 (1972).
[5] A. Haim and W. K. Wilmarth, J. Amer. chem. Soc. *83*, 509 (1961).
[6] M. B. Robin and P. Day, Advan. inorg. Chem. Radiochem. *10*, 247 (1967).
[7] D. A. Dows, A. Haim, and W. K. Wilmarth, J. inorg. nucl. Chem. *21*, 33 (1961).
[8] C. Creutz and H. Taube, J. Amer. chem. Soc. *95*, 1086 (1973).
[9] R. Glauser, U. Hauser, F. Herren, A. Ludi, P. Roder, E. Schmidt, H. Siegenthaler, and F. Wenk, J. Amer. chem. Soc. *95*, 8457 (1973).
[10] A. W. Adamson, A. Chiang, and E. Zinato, J. Amer. chem. Soc. *91*, 5467 (1969).
[11] D. F. Gutterman and H. B. Gray, J. Amer. chem. Soc. *93*, 3364 (1971).
[12] A. W. Adamson and A. Sporer, J. Amer. chem. Soc. *80*, 3865 (1958).
[13] L. Moggi, F. Boletta, V. Balzani, and F. Scandola, J. inorg. nucl. Chem. *28*, 2589 (1966).
[14] G. Ferraudi and J. F. Endicott, J. Amer. chem. Soc. *95*, 2371 (1973).
[15] J. J. Alexander and H. B. Gray, J. Amer. chem. Soc. *90*, 4260 (1968).
[16] V. Balzani and V. Carassiti, Photochemistry of Coordination Compounds, Chapter 10, and references cited therein, Academic Press, New York 1970.
[17] W. L. Waltz and A. W. Adamson, J. physic. Chem. *73*, 4250 (1969), and references cited therein.
[18] J. L. Howe, J. Amer. chem. Soc. *18*, 981 (1896).
[19] C. G. Hatchard and C. A. Parker, Proc. Roy. Soc., Ser. A, *235* 518 (1956).
[20] J. H. Bayston, R. N. Beale, N. Kelso King, and M. E. Winfield, Austral. J. Chem. *16*, 954 (1963).
[21] J. H. Bayson and M. E. Winfield, J. Catalysis *3*, 123 (1964).
[22] D. D. De Ford and A. W. Davidson, J. Amer. chem. Soc. *73*, 1469 (1951).
[23] M. B. Robin, Inorg. Chem. *1*, 337 (1962).
[24] J. Halpern and S. Nakamura, J. Amer. chem. Soc. *87*, 3002 (1965).
[25] D. F. Shriver, S. A. Shriver, and S. E. Anderson, Inorg. Chem. *4*, 725 (1965).
[26] R. A. De Castello, C. Piriz Mac-Coll, N. B. Egen, and A. Haim, Inorg. Chem. *8*, 699 (1969).
[27] R. A. De Castello, C. Piriz Mac-Coll, and A. Haim, Inorg. Chem. *10*, 203 (1971).
[28] P. B. Chock, R. B. K. Dewar, J. Halpern, and Lai-Yoong Wong, J. Amer. chem. Soc. *91*, 82 (1969).
[29] P. S. Braterman, J. chem. Soc. (A), 1471 (1966).
[30] N. S. Hush, Electrochim. Acta *13*, 1005 (1968).
[31] G. L. Simon, A. W. Adamson, and L. F. Dahl, J. Amer. chem. Soc. *94*, 7654 (1972), and references cited therein.
[32] M. D. Glick, J. M. Kuszaj, and J. F. Endicott, J. Amer. chem. Soc. *95*, *5097* (1973).

(Eingegangen am 10. Dezember 1974) E 3060